

# PATENT SPECIFICATION

## NO DRAWINGS



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### COMPLETE SPECIFICATION

#### Detergent Films

- I, ROBERT JOHN ANDERSON, of 32, Wilber Terrace, Bloomfield, County of Essex, State of New Jersey, United States of America, and a citizen of the United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to novel cleansing film compositions and to methods of producing same. More particularly, the present invention relates to a method of preparing a novel dry unsupported water-soluble cleansing film or leaf.
- Heretofore, the inadequacy of soap in the form of a cake or bar, for many purposes has been recognized and a more desirable method of dispensing a quantity sufficient for a single use has been sought. One of the methods previously suggested has been to produce sheets or leaves containing a soap in sufficient quantity for a single use. For example, it has been proposed to treat paper with soap, but the paper base is unsatisfactory because it is not stiff enough to aid in the washing and it disintegrates into a mass of loosely held fibres. Methyl cellulose has been suggested as a base for the preparation of soap leaves which tend towards stability in hot water, but dissolution is so low even in hot water as to result in a semi-solid residue remaining after use.
- In Specification No. 645,752 there is described and claimed a method of obtaining cleansing compositions in solid form, e.g. in ribbon, sheet or flake form, which comprises coagulating an aqueous dispersion of cellulosic material, such as methyl cellulose, ethyl cellulose, hydroxyalkyl cellulose or an alkali metal salt of a carboxyl-alkyl cellulose, in the presence of a detergent, and drying the product. For the production of the composition in the form of cakes glycol or glycerol may be added as a plasticizer for the cellulose derivative.
- According to the present invention there is provided a solid cleansing composition in the form of flexible, self-supporting film which can be cut to any desired shape or size, suitable, for example, for a single use, and which is readily and completely soluble in cold, warm or hot water, in sea-water, and in hard or soft water. For this purpose I use a cellulose ether base, namely a hydroxyethyl cellulose or an alkali metal or ammonium salt of carboxymethylcellulose, together with a plasticizer therefor, namely a liquid saturated acyclic alcohol, and an organic detergent, which can be continuously produced in the form of an unsupported film or leaf suitable for a single use. The film prepared in accordance with the present invention possesses the property of immediate solubility in water either hot or cold and avoids the drawbacks to which detergent films made from polyvinyl alcohol, methyl cellulose and the like are liable. My compositions also possess tensile strength and flexibility sufficient to be cast into film and dispensed in the form of reels. In appearance, these films present a smooth, firm, flexible plastic quality having, however, the unique and distinctive property, as noted above, of complete and rapid solubility in water.
- This film is normally prepared from a mixture formed of 33 parts to 67 parts by weight of hydroxyethyl cellulose of a water-soluble alkali metal or ammonium salt of carboxymethyl cellulose, together with 25 parts to 55 parts of a suitable organic detergent having a pH value of 7 to 10, and 15 to 30 parts of liquid, saturated acyclic alcohol as plasticizer. A preferred apportionment of ingredients is 40 parts to 50 parts of hydroxyethyl cellulose or alkali metal salt of carboxymethyl cellulose, 40 parts to 50 parts

[Price 4s. 6d.]

Price 5s. 0d.

Price 7s. 6d.

of detergent and about 15 parts to 30 parts of plasticizer. The terms "parts" and percentages as used throughout this specification unless otherwise explicitly indicated, refer to parts and percentages by weight of the total solid ingredients of the film composition.

While either hydroxyethyl cellulose or a water-soluble ammonium or alkali metal salt of carboxy methyl cellulose (e.g., the sodium or potassium salt thereof) is operative as the base material in the practice of the present invention, sodium carboxy methyl cellulose is preferred, and particularly that having a substitution of at least 0.3 to 1.2 and usually from 0.65 to 0.95; substitution referring to the average number of sodium carboxy methyl groups per anhydroglucose unit if the cellulose structure, each unit having three reactive hydroxy groups (i.e. if complete substitution of cellulose were obtained the substitution number would be 3.0). These base substances in addition to being rapidly water-soluble, should possess a maximum concentration and minimum viscosity, thus the viscosity thereof should not exceed 1000 centipoises (cps) and most desirably should be in range of from 10 cps to 750 cps. The term "viscosity" as employed herein is expressed as the logarithm of the viscosity in centipoises at 25° C. of a 2 per cent aqueous solution of the carboxymethyl or hydroxyethyl cellulose employed.

The synthetic organic detergents for use in the present compositions are preferably anionic and those having a pH in the range of about 7 to 10 and preferably of from 8 to 10. Illustrative of these detergents are sulphonated long chain acid amide derivatives, fatty acid amide polyglycolates, sulphates or long chain aliphatic alcohols and water-soluble alkali metal salts of alkyl and alkylaryl sulphonates.

Illustrative of the water-soluble alkali metal salts employed in the practice of this invention are sodium laurate, sodium palmitate, sodium oleate, sodium stearate and sodium myristate. Gardinol-type detergents ("Gardinol" is a Registered Trade Mark), e.g. those sold under the Trade name "Duponol", are particularly suitable. These are prepared from a mixture of the sodium salts of sulphated fatty alcohols by reducing the mixed fatty acids of coconut oil or of cottonseed oil and of fish oils. Natural waxes such as spermaceti, wool fat, and beeswax can be similarly reduced and employed for this purpose. Similarly, the term "sodium lauryl sulphate" employed herein is intended to encompass the sodium salts of a mixture of about 15 per cent octyl and decyl alcohol mixture, 40 per cent lauryl alcohol, 30 per cent myristyl alcohol and 15 per cent cetyl, steryl and oleyl alcohols. Other detergent materials suitable for use herein are, as noted above, the water-

soluble alkali metal salts of sulphonated and alkylated benzene or phenol. In such alkylaryl compounds, the alkyl groups should contain from 12 to 18 carbon atoms, e.g. sodium octadecylbenzenesulphonate, sodium dodecylsulphonate, and sodium tetradecylbenzenesulphonate. Detergents of this particular class are available on the market under the Trade name "Nacconol". Anionic surface-active detergents are particularly preferred because of their rapid emulsification, solubility in hard water, stability to heat and resistance to rancidity. Less preferred classes of detergents which can also be employed, most desirably in combination with an anionic wetting agent, the latter constituting at least 5.0 per cent by weight of the detergent component in the film composition, are non-ionic detergents and in addition the cationic detergents such as, for example, cetyl trimethyl ammonium bromide or *p*-tert.-octylphenoxymethoxyethyl dimethyl benzylammonium chloride. This latter class of detergents, while less preferred as detergents are useful in that they impart an antiseptic activity to the dried film.

The plasticizer selected for use herein is a liquid saturated acyclic alcohol, substituted or unsubstituted containing normally not in excess of six hydroxy groups. Illustrative of these are glycerol, diglycerol, glycerol  $\alpha$ -monomethyl ether, glycerol monochlorohydrin, 1, 2, 6-hexanetriol, ethylene glycol, propylene glycol, 2,3-butylene glycol, 2-nitro-2-methyl-1,3-propanediol and ethanalamines such as 2,2-dihydroxydiethylamine and 2-hydroxyethylamine.

In addition, it is desirable in certain instances such as are described hereinbelow to employ an additional water-soluble non-ionic surface active agent to assist in preventing the dried film from adhering to the surface and capable of effecting the release of the dried film composition therefrom. Suitable agents for this purpose are the hydrophilic polyoxyalkylene derivatives of fatty acid mono-esters of the mono-ethers of a polyhydroxy acyclic saturated alcohol, e.g. a hexahydric alcohol, having, desirably, a viscosity in the range of 200 to 500 centistokes and a pH in 5 per cent aqueous solution normally not in excess of 7 and not less than 5.

Illustratively, mannitol when heated with palmitic acid in the presence of a small quantity of alkali e.g. sodium hydroxide, as catalyst, yields mannitan palmitate. This compound is both a mono(inner) ether of mannitol and a mono-ester of palmitic acid. On being treated with ethylene oxide, propylene oxide or other lower alkylene oxide it can be made water-soluble by the introduction of a plurality of the corresponding oxyalkylene groups into the molecule. Other hexahydric alcohols such as, for example, dulcitol and sorbitol may also be used. Similarly, other fatty acids, and preferably those containing

12 to 18 carbon atoms, can be substituted for palmitic acid, e.g. lauric acid, myristic acid, stearic acid, oleic acid. Specific examples are polyoxyethylene (2) sorbitan mono-oleate, polyoxyethylene (20) sorbitan mono-stearate, polyoxypropylene (20) mannitan monolaurate and the like. This invention is not, however, limited to the use of mono inner ethers. By inner ether is meant those ethers wherein a molecule of water has been eliminated between two hydroxyl groups in the same molecule and an ether linkage has resulted. The analogous polyoxyalkylene derivatives of a normal ether can also be employed. By a normal ether, as the term is employed herein, is meant those ethers wherein two molecules of the polyhydric alcohol are joined by means of an ether linkage.

The inclusion of surface active agents while particularly appropriate for the preparation of the film or leaf of our invention by many procedures such as where a metal drying pan or belt is employed for drying, is less preferred; its presence contributing to a lessening of the film strength and an increase in the cost of film production. When required for efficient production it should not exceed ten per cent of the total solids of the film composition, normally where included it will be present in amounts of one to five per cent of the solid components of the composition.

A film composed of polytetrafluoroethylene which resin is described by M. M. Renfrew and E. E. Lewis, *Industrial and Engineering Chemistry*, Vol 38, page 870 (1946); R. C. Doban et al, *Society of Plastic Engineers Journal*, Vol. 11, page 9, (November 1955) and P. E. Thomas et al, *Society of Plastic Engineers Journal*, Vol. 12, page 6 (June 1956) is, however, particularly desirable as the drying surface for the compositions of my invention; and indeed represents a significant improvement over other procedures employing, for example, a metal surface or the like.

A glass-coated fabric thereof (e.g. that sold under the Registered Trade Mark "Armolon", a metal-coated platen or belt, or alternatively a heat-bonded film (e.g. as described by P. J. Wayne and W. M. Bruner, *Society of Plastic Engineers Journal*, Vol. 11, page 10 (December 1955) attached to an undersurface of a material which is heat resistant at the highest processing temperature for the detergent film (e.g. 300° F.) and chemically inert, can by way of illustration be employed. Where coated on a glass or metal surface the thickness of polymer is usually in the range of 3 to 10 mils. For heat-bonding to another surface composed of another material or poly(tetrafluoroethylene) or freely supported on an under surface e.g. of metal or canvas, thicknesses of from 20 mils or less to 120 mils are normally employed. Films in excess of this thickness and pre-

ferably in excess of 200 mils are self-supporting.

Polytetrafluoroethylene, particularly that having a density of .035 and in the range of 0.30 to 0.40 and a softening point of about 620° F. is preferred because of the non-adhering surface it presents to the dried detergent film permitting ease of removal of the film therefrom. This property is so marked that non-ionic surface active agents included in the film composition for release thereof from the drying surface can be, and preferably are, omitted.

The rate of solubility of the composition of my invention while rapid, as noted can in certain instances be increased (e.g. particularly where hydroxy ethyl cellulose is employed) by increasing the porosity of the film composition. This is accomplished by introducing therein a solid dispersing agent which will assist in dissolving the film in water. Suitable dispersing or diluting agents are the mixed aluminium, magnesium and calcium silicates, for example, in clays, such as bentonite, kieselguhr, diatomaceous earth and talc. Hydrated aluminium silicate or hydrated magnesium silicate can also be employed. These substances are readily swollen by water and are easily dispersed in aqueous media. These silicates should not, of course, contain any solid or non-dispersible substances which might act as abrasives. It is normally convenient to incorporate these silicate clays in the fluid film composition with the other ingredients as an aqueous dispersion, e.g. a dispersion containing 80 to 90 per cent water by weight of clay.

Alkaline agents, such as for example, the water-soluble alkali metal salts of carbonates and the corresponding tetra-salts of pyrophosphoric acid or boric acid, e.g. sodium carbonate, potassium carbonate, borax, tetra-sodium pyrophosphate, are also useful swelling agents which increase the porosity of the film composition and thus accelerate the dissolution thereof in water. Indeed these latter substances aid in releasing the dried film from the heated or drying surface where the said surface is other than polytetrafluoroethylene, e.g. metal.

Such porosity-conferring agents whether clay, alkaline inorganic dispersant or the like, should not exceed five per cent by weight of the total composition. Indeed, smaller quantities in the range of 1 to 2 per cent are more usually employed.

In addition perfume and colouring matter can be included, optionally, together with a disinfectant or antiseptic material or the like. Such added substances will ordinarily not exceed a total of one per cent by weight of the final film composition.

The quantity of water in which are dissolved all of the ingredients (prior to formation of the solid film) should be just suffi-

cient to keep all of them in solution at atmospheric or room temperature. Usually this quantity of water will be about 2 and preferably 4 to 10 times the total weight of solid ingredients. The carboxy methyl cellulose constituent is preferably dissolved initially in the water, warmed to a temperature of from 70° F. to 100° F. and agitated at high speeds. When substantially complete solution has been obtained the remaining components, i.e. detergent, plasticizer and other constituents as described above, are added with slower speed agitation. This will result in lessening the sudsing tendency of the aqueous composition. Sudsing is undesirable in that it tends to reduce the tensile strength of the dried film. Alternatively, or if desired in addition, this difficulty can be overcome by adding a small proportion (e.g. up to 5 per cent) of a low-boiling alcohol, such as ethyl, isopropyl, or *tert.* butyl alcohol, to the solution. These alcohols have boiling points which are lower than that of water, so that such liquids will be evaporated during conversion of the aqueous solution into a solid film.

In making solid films, the aqueous solution is spread on to a heated surface in the form of a liquid film (normally of a thickness of .002 to .08 inch depending on the amount of water and other volatiles present) and water as well as other volatile liquids, if present, evaporated therefrom until the film becomes solid. The rate at which the liquid is allowed to flow on to the heated surface and the rate at which evaporation is effected are factors which are not narrowly critical but are well within the skill of the art. The temperature of the heated surface may vary from 150° F. to 200° F. and no actual boiling should be permitted during evaporation of liquid from the aqueous solution. Solid film formation may be a batch process, as for example, by placing the liquid composition in a flat heated container and heating the latter. Or, the operation can be made continuous, for example, by allowing the aqueous solution to flow continuously on to a heated moving surface (e.g. a rotating drum or cylinder and continuously stripping the solid film therefrom as described hereinafter.

In drying the liquid compositions of the invention, it has been found that this operation is effected most advantageously, as noted at a temperature within the range of 150° F. to 200° F. although lower temperature, e.g. 130° F. and higher temperature, e.g. 300° F. can also be employed. These temperatures, it is to be understood, are temperatures at the surface of the film. The drying period normally extends from 5 minutes to 10 minutes. Drying can, however, be effected even at room temperature, i.e. by spontaneous evap-

oration of water from the liquid mass, nevertheless such operations are slow and are not feasible for continuous film formation. Within the temperature range mentioned above (i.e. 150° F. to 200° F.) evaporation of water (or other volatile liquids) from the liquid or wet mass is sufficiently rapid to permit film formation to be performed as a continuous operation. It is desirable to avoid a temperature as high as the boiling point of water, otherwise the films (after drying) may contain a large number of holes or pockets due to steam formation during drying. In other words, in my process, drying is essentially a removal of water vapor from the surface of a liquid film without formation of any substantial proportion of steam or other gases within the film.

Drying of the liquid film is continued until its water content is about 5 to 10 per cent of the weight of the film. A substantially smaller proportion of water than 5 per cent gives rise to films which are too brittle for my purpose. A substantially larger proportion than 10 per cent of water furnishes a film which is too soft and not readily handled.

Dried films whose thicknesses vary from about 0.001 to 0.008 inch are suitable for use as soap films and leaves. If the thickness is substantially less than 0.001 inch, the film is brittle and also lacking in strength and therefore breaks easily. If the thickness is substantially greater than about 0.008 inch, then the film becomes too stiff and is not easily worked. Moreover if the film is too thick its rate of solution in water may become undesirably slow. Preferred thicknesses are in the range of .003 to .004 inch.

Flexible, self-sustaining detergent film as described herein can be cut into sheets two to four inches square or more and if desired a number of such sheets or leaves bound into booklets which can be conveniently carried in the pocket or purse, and a sheet removed from the booklet as required. The film made in the form of continuous strips, can be wound on reels for installation in suitable dispensing devices in lavatories and the like. The desired length of strip is torn off at the time of use. If desired, suitable perforations can be provided at intervals across the continuous strip of film to facilitate separation of a portion of said film from the ruled strip. Adjacent sheets of this film can also be used as a container wherein soap crystals for "bubble baths" and the like in suitable quantity for a single use are incorporated. The edges of said container formed from sheets of the subject detergent film are sealed by heat and pressure and opened only upon dissolution in the bath water.

The following examples are further illustrative of the invention.

## EXAMPLE 1

Sodium carboxy methyl cellulose (100—	
200 cps. substitution #0.65—0.85) - -	9.6 grams
Water - - - - -	100.0 grams
Sodium lauryl sulphate - - - - -	10.0 grams
Glycerine - - - - -	1.5 grams

This composition is fed to a hopper from which a film approximately .004 inch in thickness passes to an endless moving belt of polytetrafluoroethylene, as characterized in Table 1 above and having a tensile strength of about 13000 lb/sq. in. as measured by ASTM Procedure D638-52T and a thickness of about 250 mils. The detergent film then traverses a heating zone wherein the temperature is graded from an initial temperature of 120° F. to a final temperature zone of 200° F. at a rate sufficient to evaporate about

95 per cent of the water from the film. The dry film remaining on the belt is then removed from the belt and taken up on a roll. Ready release of the dry film is due to the non-adhering polytetrafluoroethylene resin or resin-coated belt. The film obtained exhibits good sudsing quality, is sufficiently flexible to permit bending, and when two or more films are placed one upon the other there is no sticking of one film to the one immediately adjacent to it.

## EXAMPLE 2

Sodium carboxy methyl cellulose (40—90	
cps; substitution #0.65—0.85) in a 9 per	
cent aqueous solution - - - - -	4.0 grams
Sodium tetradecylbenzene sulphonate -	2.0 grams
Propylene glycol - - - - -	1.0 gram
Water - - - - -	35.0 grams

A soap leaf is prepared from this composition in the manner described in Example 1.

## EXAMPLE 3

The following composition also yields a film or leaf when dried according to the process of Example 1.

Sodium carboxy methyl cellulose (40—90	
cps; substitution #0.65—0.85) - - -	9.6 grams
Water - - - - -	90.0 grams
Sodium tetradecylbenzene sulphonate -	10.0 grams
Glycerine - - - - -	2.0 grams
Sodium carbonate - - - - -	1.0 gram

## EXAMPLE 4

Hydroxy ethyl cellulose (700—800 cps)	10.0 grams
Sodium myristate - - - - -	10.0 grams
Glycerol monochlorohydrin - - - - -	2.0 grams
Tetra-sodium pyrophosphate - - - - -	0.3 gram

This composition is converted to a film of .004 inch thickness according to the process of Example 1.

## WHAT I CLAIM IS:—

1. A solid composition in the form of a flexible, self-supporting film of substantially uniform thickness, comprising a water-soluble hydroxyethyl cellulose or an alkali metal or ammonium salt of carboxymethyl cellulose together with a saturated acyclic alcohol as plasticizer therefor and an organic detergent.

2. A solid composition as claimed in Claim 1, comprising 33—67 parts of the cellulose derivatives, 25—55 parts of an organic detergent having a pH value of 7—10, and a liquid saturated acyclic alcohol as plasticizer.

3. A solid composition as claimed in Claim 1 or Claim 2 wherein the thickness of the film is 0.001—0.008 inch and the water con-

tent is 5 to 10% by weight of the composition.

4. A solid composition as claimed in any of the preceding claims, wherein the composition contains an additional non-ionic surface active agent.

5. A solid composition as claimed in Claim 4, wherein the additional non-ionic surface active agent has a viscosity of 200—500 centistokes.

6. A solid composition as claimed in any of the preceding claims containing in addition up to 5% by weight of an inorganic dispersing agent, e.g. bentonite, kieselguhr, diatomaceous earth, talc, hydrated aluminium silicate of hydrated magnesium silicate.

7. Process for the production of solid compositions in the form of films which comprises pouring an aqueous solution of hydroxyethyl cellulose or of an alkali metal

5 or ammonium salt of carboxymethyl cellulose, a saturated acyclic alcohol and an organic detergent on to a plane surface preferably of polytetrafluoroethylene, lowering the water content of the solution to not less than 5% and removing the solidified film from the plane surface.

10 8. Process as claimed in Claim 7 wherein the aqueous solution contains 33—67 parts of hydroxyethyl cellulose or of an alkali-metal or ammonium salt of carboxymethyl cellulose, 25—55 parts of an organic detergent having a pH value of 7—10, a liquid saturated acyclic alcohol as plasticizer for the cellulose derivatives and an excess of water.

15 9. Process as claimed in Claim 7 or 8 wherein the film is caused to have a thickness of 0.001 to 0.008 inch.

20 10. Process as claimed in any of Claims 7—9 wherein the aqueous solution is poured on to a moving surface, preferably of polytetrafluoroethylene, and preferably at 150—200° F.

25 11. Process as claimed in any of Claims 7—10, wherein an additional non-ionic sur-

face active agent is added to the aqueous solution.

12. Process for the production of solid compositions in the form of films which comprises pouring an aqueous solution of 33—67 parts of hydroxyethyl cellulose or an alkali-metal or ammonium salt of carboxymethyl cellulose, 25—55 parts of an organic anionic detergent having a pH value of 7—10, and a liquid saturated acyclic alcohol, on to a surface of polytetrafluoroethylene where it is heated at 130—300° F. for a period sufficient to form a dried film and removing the film from the polytetrafluoroethylene.

13. Process for the production of solid compositions and films therefrom substantially as described with reference to each of the foregoing examples.

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